

Effect of solvents on the properties of ZnO thin layers obtained by sol gel dip coating process

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Abstract

Undoped Zinc Oxide (ZnO) thin films have been grown on glass substrates by sol gel process associated with dip coating using two different solvents, ethanol and 2-methoxyethanol. The effects of these solvents on structural and optical properties of ZnO thin films have been studied. Crystallinity and surface morphology of the ZnO films were analyzed using X-ray diffractometry (XRD), Raman microscopy and atomic force microscopy (AFM). The optical properties were determined by means of photoluminescence spectroscopy (PL) and Fourier transform infrared spectroscopy (FTIR). The experimental results revealed a better crystalline quality and ultraviolet emission performance and a higher surface roughness for ZnO thin films prepared with 2-methoxyethanol.

Keywords: ZnO thin films; Sol-gel; FTIR; Photoluminescence; Raman; Spectroscopy, XRD.

1. Introduction

Zinc oxide (ZnO) is an oxidic compound naturally occurring as the rare mineral zincite, which crystallizes in the hexagonal wurtzite structure $Pb\bar{3}mc$ [1]. ZnO is n-type semiconductor material with a wide band gap of 3.3 eV and a large exciton binding energy of 60 meV [2], in addition it has specific properties such as low costs, non toxicity, high transparency in VIS/near IR spectral region [3]. These numbers of properties give ZnO increasing attention in the research community such as varistors, light-emitting diodes (LEDs), optoelectronic devices and conductive gas sensors [4-7]. Many techniques have been used to synthesize ZnO thin films, such as pulsed laser deposition, atomic layer deposition, RF magnetron sputtering, chemical vapor deposition, plasma-assisted molecular beam epitaxy (MBE) and sol-gel process [7-13]. Among them, the sol-gel technique offers the possibility of preparing a small at low cost for technological applications. The usual starting materials

of the sol-gel process are metal alkoxides that are hydrolyzed to form a sol, solvents such as 2-methoxyethanol, ethanol and isopropanol, stabilizers can also be added like monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). It is also well known that the properties of ZnO films deposited by sol-gel technique change depending on the nature of the starting materials mentioned previously. However, few studies have been devoted to the study of the influence of solvent upon films properties [14-15].

In this work, ZnO films grown on glass substrates using sol-gel method were fabricated and the effects of solvent on the structural and optical properties of the films were intensively investigated.

2. Experimental procedure

In order to deposit undoped ZnO thin films on glass substrates using sol-gel process, the precursor solutions were prepared from zinc acetate dehydrate

(Zn(CH₃COO)₂·2H₂O), solvent (2-methoxyethanol (C₃H₈O₂, 99.5%) or ethanol) and stabilizer (Diethanolamine (DEA)). The sols were prepared by dissolving of zinc acetate dehydrate in 2-methoxyethanol or absolute ethanol, in which DEA was subsequently added to obtain a transparent solution and to keep the solution stable for dip-coating process. The molar ratio of DEA to zinc acetate was 1.0 and the zinc acetate concentration was 0.7M. Then the resultant solution was magnetic stirred at 60°C for 2h until it become clear and homogeneous to serve as the coating solution after aging for more than 24 hours at room temperature. Undoped ZnO thin films were deposited on pre-cleaned glass substrates using the dip-coating technique at a speed of 3cm/min. These substrates were cleaned ultrasonically initially by ethanol then by acetone and finally with de-ionized water. Between each deposition process, the substrates were dried at 300°C in the case of 2-methoxyethanol and 60°C in the case of ethanol for 10 minutes in air. This process was repeated eight times to obtain the desired thickness. Finally, the samples were annealed at 500°C in air for 2 hours.

The crystalline structures of the samples were analyzed by an X-ray diffractometer (XRD, Bruker D8 Advance) with Cu K α radiation. During the measurement, the current and voltage of XRD was maintained at 20 mA and 40 kV, respectively. The surface morphology was evaluated by Atomic Force Microscopy (Pacific Nanotechnology Advancing Nanotechnology). Raman spectra of the samples were recorded on a Bruker Raman spectrometer using a 523 nm wavelength YAG laser.

The optical properties of the deposited films were investigated using FTIR and photoluminescence. FTIR measurements were performed in the spectral region 400-4000 cm⁻¹ using a Fourier transform infrared spectrometer Jasco (FT/IR-6300). PL spectra were collected in the wavelength region of 300-850 nm. The samples were excited by Hg arc lamp using 315 nm as the excitation source.

3. Results and discussion

3.1. XRD (X-ray diffraction)

The crystallinity of sol-gel derived ZnO thin films were identified by X-ray diffraction. Fig.1 shows the XRD patterns of ZnO thin films prepared by different solvents (2-methoxyethanol and ethanol). These patterns correspond to three diffraction peaks of polycrystalline ZnO at (100), (002) and (101) planes. The result reveals that ZnO gel films annealed at 500°C have a hexagonal wurtzite structure. The intensity of the (002) peak is higher than others peaks, so the predominant orientation is (002) in the two cases.

Table1 summarizes the intensities of different peaks for ethanol and 2methoxyethanol.

The average crystallite size D is obtained using the Debye-Scherrer formula [16]

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where: $\lambda = 0.15406$ nm is the wavelength of X-ray, β is the full width at half maximum (FWHM) of the peak and θ is the Bragg's angle. The crystallite sizes corresponding to preferred orientation of crystalline thin films are reported in table1.

We remark that the crystallite size value in the case of the ZnO films prepared with ethanol is smaller than those prepared with 2-methoxyethanol.

Solvent	(hkl)	2 θ (degree)	Intensity (a.u.)	FWHM (degree)	Crystallite size (nm)
2 Methoxy-ethanol	(002)	34.72	90.12	0.26	33.1
Ethanol	(002)	34.78	42.72	0.37	22.9

Table1. hkl, 2 θ , intensity, FWHM and crystallite size values for the ZnO thin films

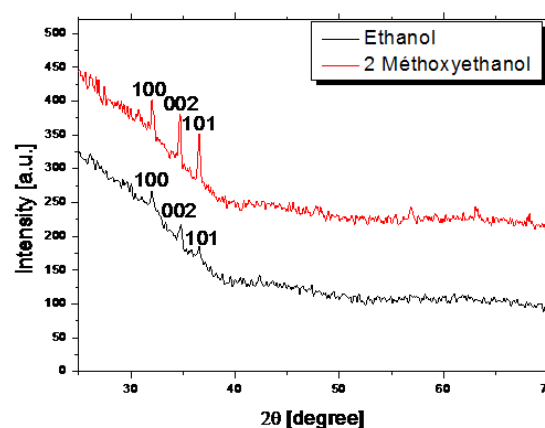


Fig.1. XRD patterns of ZnO thin films annealed at 500°C for 2h

3.2. AFM (Atomic Force Microscopy)

Fig.2 shows the three dimensional surface morphology images of ZnO thin films prepared from different solvents. The scanning area is 0.78×0.78 μ m². We can remark for these images that we have obtained a fine grains in the two cases, whereas the surface is roughness in the case of 2-methoxyethanol. The root mean square (RMS) roughness is 7.86 nm and 2.17 nm in the case of 2 methoxyethanol and ethanol, respectively.

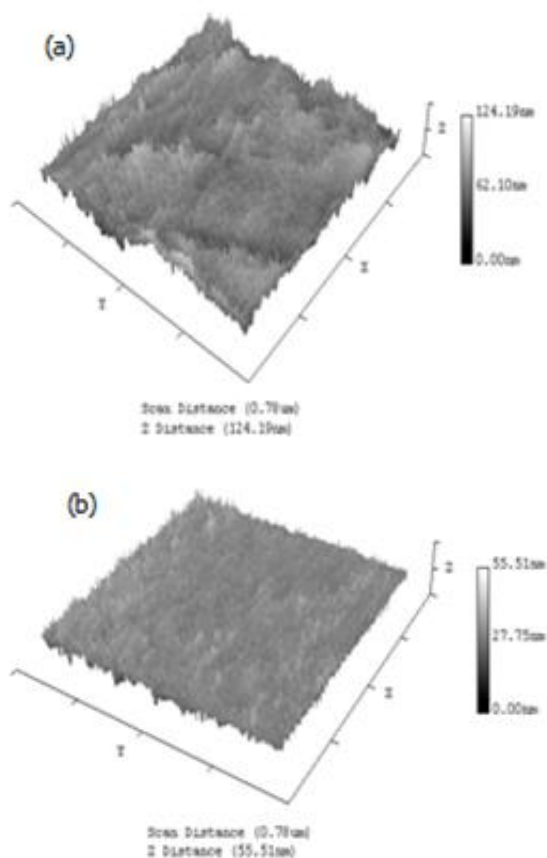


Fig.2. AFM images of ZnO thin films prepared with: (a) 2-Methoxyethanol (b) Ethanol

3.3. Raman spectroscopy

Fig.3 shows the Raman spectrum of undoped ZnO thin films, Wurtzite-type ZnO belongs to the space group $P63mc$, the zone center optical phonons can be classified according to the following irreducible representation: $\Gamma_{opt}=A_1+E_1+2E_2+2B_1$, where B_1 modes are silent, A_1 and E_1 are polar modes, both Raman and infrared active, while E_2 modes (E_2 low and E_2 high) are non polar and Raman active only.

In the two cases we have observed the first peak located around 99 cm^{-1} , it is related to the E_2 (low) phonon frequency of the ZnO wurtzite structure [17-18]. The second one is the LO mode at 560 cm^{-1} , which is contributions from both the A_1 (LO) and E_1 (LO) modes (LO scattering mode) due to random crystallite orientation [19]. Whereas another vibration band is observed in the case of 2-methoxyethanol located at 438 cm^{-1} correspond to E_2 (high) mode is predominately associated with vibrations of oxygen sublattice, is typical for ZnO hexagonal structure [20]. The presence of this mode indicate the crystallinity of the thin films prepared

with 2-methoxyethanol is better, which confirm the results observed by XRD analysis [21].

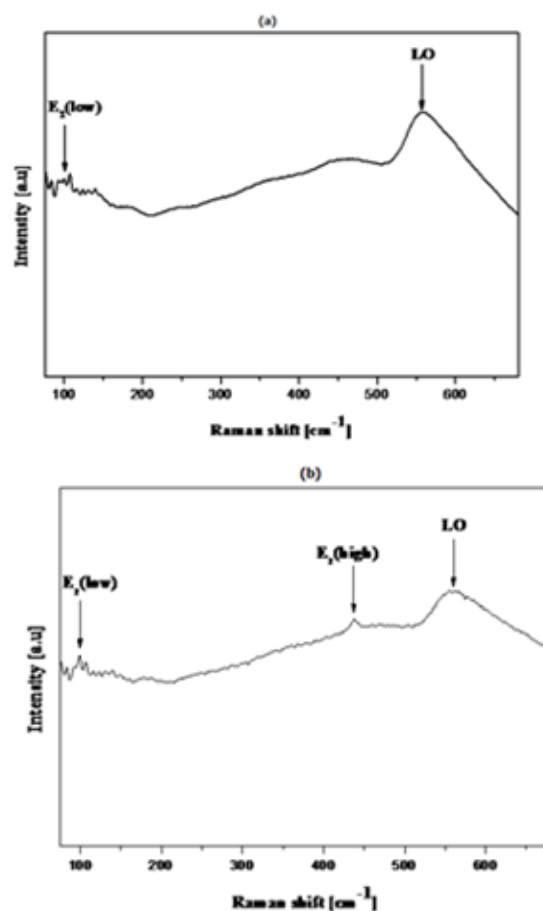


Fig.3. Raman spectrum of undoped ZnO thin film prepared with: (a) Ethanol (b) 2-Methoxyethanol

3.4. FTIR (Fourier transform infrared spectroscopy)

The FTIR analysis of ZnO thin films synthesized with different solvents are shown in Fig.4.

The FTIR spectrum for the undoped ZnO thin films shows no characteristic functional groups in the low frequency region except a weak absorption around 2350 cm^{-1} [22-23]. This weak absorption is probably due to an existence of CO_2 molecules in air. Another strong peak is observed at 890 cm^{-1} is observed, this peak is resulting from C-O vibrations [23]. The feature appearing between 520 and 770 cm^{-1} , which comprises of several peaks, are attributed to the stretching modes of Zn-O [23-25]. In the two cases, we have obtained the same peaks but there is a slight shift due to the change in the morphology of these films

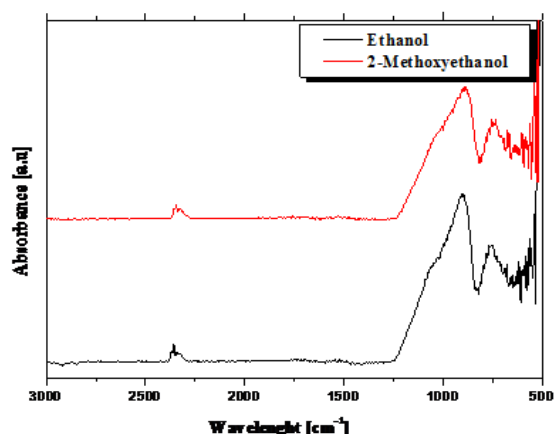


Fig.4. FTIR spectra of ZnO thin films annealed at 500°C for 2h

3.5. PL (Photoluminescence spectroscopy)

Photoluminescence is a powerful tool to identify surface, interface, and impurity levels and to evaluate alloy disorder and interface roughness. The intensity of the photoluminescence signal provides information on the quality of surfaces and interfaces by the determination of optical active defects and relaxation pathways of excited states [26-27]. The luminescence spectrum of ZnO thin films prepared by sol-gel method is shown in Fig.5. The PL spectra in all samples exhibit two emission peaks, an intense near band-edge (NBE) emission located at 380 nm, due to free exciton emission, and a broad band one around to 530 nm related to the green emission. The origin of the green luminescence is usually attributed to emission related to grain boundary defects and other interior defects such as oxygen vacancy (VO) and impurities [28]. The intensities of these peaks are higher in case of 2-methoxyethanol than those in case of ethanol, giving good ZnO quality with 2-methoxyethanol.

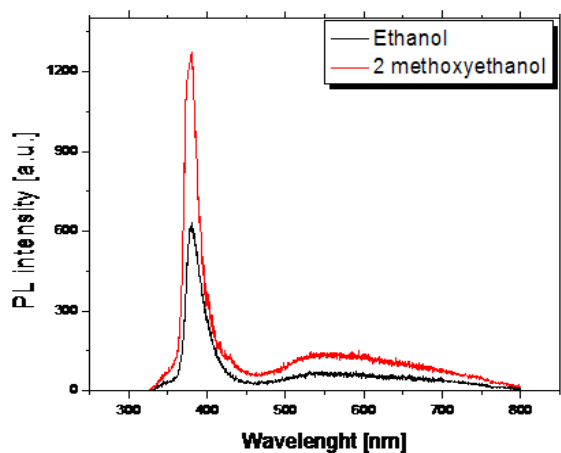


Fig.5. PL spectrum of ZnO thin films annealed at 500°C for 2h

4. Conclusion

Transparent and high quality undoped ZnO thin films were deposited on glass substrate using sol-gel dip coating method. We have carried a comparative study of structural and optical properties of ZnO thin films prepared from two different solvents. XRD spectra indicate that all films exhibit wurtzite hexagonal crystal structure with preferred orientation growth along (002) plane. AFM surface analysis revealed that films surface is smoother in sample deposited with ethanol as solvent than in that prepared with 2-methoxyethanol. The presence of E₂ (high) mode indicate the better crystallinity of thin films prepared with 2-methoxyethanol. Photoluminescence spectra of these films exhibit two peaks due to free exciton emission and to oxygen vacancies in ZnO.

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